PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 19 July 2000 (19.07.00)	
International application No. PCT/GB99/03958	**Applicant's or agent's file reference** PFC 1436 PCT
International filing date (day/month/year) 29 November 1999 (29.11.99)	**Priority date** (day/month/year) 01 December 1998 (01.12.98)
Applicant GRAY, Peter, Geoffrey et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

23 June 2000 (23.06.00)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Pascal Piriou
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
PFC 1436 PCT		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB 99/03958	29/11/1999	01/12/1998
International Patent Classification (IPC) or national classification and IPC		
C01B3/58		
Applicant		
JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 8 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consists of a total of 2 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
23/06/2000	09.03.2001
Name and mailing address of the IPEA/	Authorized officer
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/03958

I. Basis f th report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-6	as originally filed				

Claims, No.:

1-14	as received on	18/09/2000	with letter of	12/09/2000	

Drawings, sheets:

1/1	as originally filed

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

see separate sheet

4. Additional observations, if necessary:

V. Reasoned statement under Articl 35(2) with regard t novelty, inventive st p or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 1-14
	No:	Claims
Inventive step (IS)	Yes:	Claims
	No:	Claims 1-14
Industrial applicability (IA)	Yes:	Claims 1-14
	No:	Claims

2. Citations and explanations

see separate sheet

VII. C rtain defects in the international application

The following defects in the form or contents of the international application have been noted:

se separate sheet

Re Item I

Basis of the report

1. With his reply to the first written opinion the applicant has filed a completely new set of claims, without referring to this fact in his letter of reply. Of course, due to this omission to mention the new set of claims, also no basis for the amendments has been indicated.

   This is highly objectionable, because it puts a high burden on the examiner to find all the amendments, and to further find their basis in the application as filed.

2. Some of the amendments proposed by the applicant go beyond the application as filed (Article 34(2)(b) PCT).

2.1. Claim 6 defines that the central jacket is connected via a coolant circuit to a circulating pump. The basis for this amendment seems to lie in page 3, lines 11-13, where a water circuit and a circulating pump are disclosed.

   This has now been generalised to cooling circuit in general. Subject-matter has been added.

   It is admitted that on page 2 it is mentioned that other coolants can be used. However, the circulating pump seems only to be disclosed in relation to water being the coolant.

2.2. Claim 10 defines that the gas mixing means comprise annular mixing vanes or discs. The expression "annular mixing vanes or discs" can only be found on page 3, lines 20 and 21. This passage discloses that the first mixer is a static mixer, whereas the other mixers are alternating "annular mixing vanes or discs".

   The claims now specifies that also the first mixer is an "annular mixing vane or disc", which was not disclosed in the application as originally filed. Subject-matter has been added.

2.3. Since the applicant has not given any indication of the basis for the amendments,

the final decision on the allowability of the amendments is deferred to the regional phase.

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step r industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: WO-A-93/19005
D2: GB-A-2075859
D3: US-A-4988431
D4: DE-A-19544895

1. The subject-matter of the present claims is novel. The subject-matter of claims 1-14 does not involve an inventive step, however (Article 33(3) PCT).

   Inventive step objections arise starting from document D1 and starting from document D4.

1.1. **Starting from document D1:**

   Document D1 discloses a reactor for the selective oxidation of carbon monoxide in the presence of hydrogen. The reactor contains two catalytic beds. Cooling coils are embedded in the 2 catalyst beds. From figure 1 it is clear that the coolant flows countercurrently to the reacting stream. The reactor has inlets for gaseous fuel and oxygen. The product from the reactor is fed to a fuel cell (see figure 1; page 9, line 3 - page 12, line 32).

   In his letter of reply of 12.09.2000, the applicant has argued that claim 1 is novel for several reasons.

   Firstly, it is argued that the present reactor is contained in a single vessel. With respect, the examiner cannot agree on this point of view, because claim 1 specifies that the reactor **comprises** a cylindrical reactor vessel, with at least one

stage. Document D1 clearly has one stage in a vessel. The presence of a second stage in a second vessel is certainly not excluded from claim 1.

Secondly, it is argued that the apparatus of document D1 does not have any mixing means. With respect, the examiner cannot agree with the applicant here. It should first be mentioned that the term mixing means is extremely broad, giving no indication what sort of mixer is meant. In any case, on page 9, lines 20-23 of document D1 disclose that the perforated support member (23) facilitates distribution of gases to all regions of the catalyst bed. Perforated support member (23), therefore, clearly functions as a mixing means.

The only difference between claim 1 and document D1, therefore, lies in the fact that in claim 1 the catalyst is supported on a metallic support, whereas in document D1 the catalyst is supported on a metal oxide support.

Document D4 discloses an apparatus for the selective oxidation of carbon monoxide. The catalysts used in this apparatus are preferably supported on a metallic support.

The person skilled in the art will certainly consider using catalysts supported on a metallic support in the apparatus of D1. The subject-matter of claim 1 does not involve an inventive step.

It is noted that similar objections can be raised starting from document D2 and document D3.

1.2. Starting from document D4:

Document D4 discloses an apparatus and process for the selective oxidation of carbon monoxide in presence of hydrogen. The apparatus has several catalytic stages, in which the catalyst is preferably supported on metallic supports. The reactor is cooled by a cooling circuit, which is connected to the outside of the reactor. From the figures, it would appear that the cooling takes place co-currently. The reactor has inlets for oxygen and for the gas to be treated and contains several static mixers to achieve mixing (and cooling) of the reactants.

The product of the reactor can be fed to a fuel cell (see figures; column 3, line 35 - column 4, line 50).

The only difference between claim 1 and document D4 lies in the fact that in claim 1 the cooling takes place countercurrently, whereas in document D4 the cooling takes place co-currently.

The skilled chemical engineer, who is the person skilled in the art in the present case, always considers both co- and countercurrent operation of heat-exchange processes.

The applicant has argued that claim 1 further differs from document D4 in the fact that in claim 1 the apparatus is cylindrical, whereas in document D4 this would not be the case. The examiner cannot agree on this point with the applicant. Although the preferred embodiment of document D4 is directed to a plate-type reactor, the use of other forms for the reactor are also disclosed according to the examiner. In any case, the choice of a cylindrical shape for a reactor is the first choice for the skilled chemical engineer, for the reasons as given by the applicant in his letter of reply to the written opinion (compact, easy manufacture).

The subject-matter of claim 1 does not involve an inventive step.

2. The subject-matter of claim 12 does not involve an inventive step.

Document D1 is considered to be the closest prior art for claim 12.

The only difference between claim 12 and document D1 lies in the fact that in claim 1 the catalyst is supported on an annular metal support, whereas in document D1 the catalyst is supported on a particulate metal oxide support.

Document D4 discloses the use of metallic supports in the selective oxidation of carbon monoxide.

The person skilled in the art will, therefore, certainly think of using a metallic catalyst support. The further choice of an annular shape of the support, seems to

be the choice from a limited number of possibilities.

The subject-matter of claim 12 does not involve an inventive step.

3. The subject-matter of claims 2-11, 13 and 14 also does not involve an inventive step.

3.1. Claims 2, 4-7 are directed to features of the cooling of the reactor, which are all well-known measures to the person skilled in the art. The subject-matter of claims 2, 4-7 does not involve an inventive step.

3.2. A recent trend in gas-phase catalytic reactions is the use monoliths as catalyst supports. The subject-matter of claim 3 does not involve an inventive step.

3.3. Both document D1 and document D4 disclose a plurality of oxidation stages. the person skilled in the art will be able to choose the optimum number of stages. The subject-matter of claims 8 and 9 does not involve an inventive step.

3.4. The mixing vanes or discs seem to be well-known mixing means. The subject-matter of claim 10 does not involve an inventive step. It is noted that the claim does not fulfil the requirements of Article 34(2)(b) PCT (see section I, above).

3.5. From the introduction of document D4 it is clear that the selective oxidation of carbon monoxide is used on synthesis gas, to make it suitable for use in a fuel cell. The subject-matter of claims 11 and 14 does not involve an inventive step.

3.6. Document D1 discloses using an inlet temperature of 320°F (=160°C; see claim 11). The subject-matter of claim 13 does not involve an inventive step.

Re Item VII

Certain defects in the international application

1. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1 and D4 is not mentioned in the description, nor are these documents identified therein.

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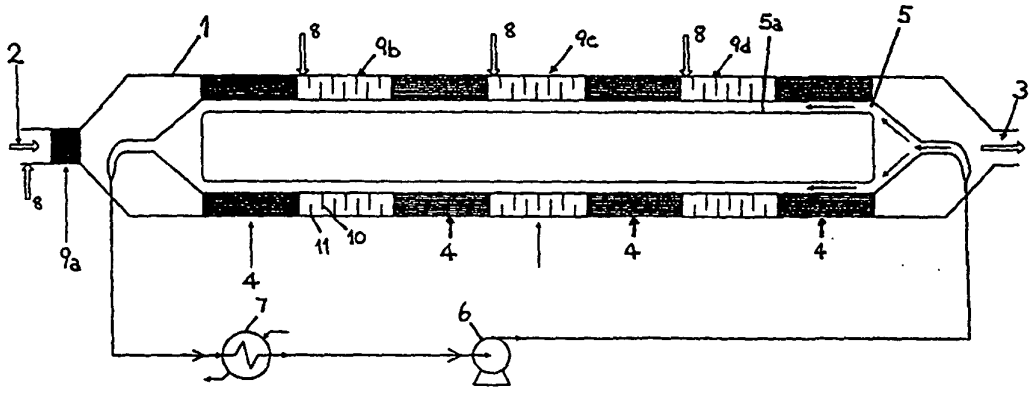

(57) Abstract

A reactor vessel (1) contains one or more selective oxidation stages and has counter-current cooling (5, 6, 7), each stage having an inlet for feedstock such as CO-contaminated hydrogen (2), an inlet for a second feedstock such as oxygen or air (8), gas mixing means (9a, 9b) and a catalytic reaction zone (4), preferably containing a metal support carrying a selective oxidation catalyst. A compact reformer with a very low pressure drop is suitable for producing hydrogen for fuel cell.

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REACTOR AND PROCESS FOR REMOVAL OF CARBON MONOXIDE FROM HYDROGEN

The present invention concerns an improved reactor, more particularly it concerns a reactor particularly adapted for and suitable for certain selective oxidation reactions.

We have previously developed certain selective oxidation processes for the removal of residual carbon monoxide in hydrogen-containing gases intended as feedstock for fuel cells. Such processes are disclosed and claimed in for example, PCT/GB98/02873. It has become well established that hydrogen-fuelled fuel cells require very low proportions of carbon monoxide, which acts as a catalyst poison and degrades performance of the fuel cell. Desirably, the amount of CO is less than 10 ppm. If a liquid fuel is reformed to form a hydrogen-containing fuel, levels of CO are produced which may vary about 0.5-5mol%, so that it becomes necessary to attenuate such CO levels. As mentioned in the above International Application, catalytic selective oxidation reactions are highly exothermic with the result that increasing reaction temperatures lead to increasing loss of valuable hydrogen due to competing reactions.

There remains a need for a catalytic selective oxidation reactor which permits good temperature control yet is simple, effective and inexpensive to manufacture. Although hydrogen "cleaned-up" by the reactor of the present invention may be used as fuel cell fuel, there are many other uses for such hydrogen. Also, although the reactor is particularly suitable for the cleaning up of reformate (which may be from methanol, other oxygenated fuels, gasoline or other hydrocarbon fuels), it is not limited to such use. Accordingly, the present invention provides a reactor for catalytic selective oxidation, comprising a reactor vessel with counter current cooling and at least one stage, each stage provided with an inlet for a first feedstock, e.g. CO contaminated hydrogen, an inlet for a second feedstock, e.g. oxygen-containing gas, gas mixing means and a catalytic reaction zone, preferably comprising a selective oxidation catalyst deposited on a substrate having good heat conduction properties.

The invention also provides a process for the removal of quantities of CO from a hydrogen feedstock by partial oxidation, comprising at least one step of admixing said

feedstock with a quantity of oxygen, passing the resulting mixture over a selective oxidation catalyst in a selective oxidation zone and recovering a hydrogen product with reduced content of CO, whilst simultaneously cooling the selective oxidation zone, preferably to maintain the selective oxidation zone at a temperature in the range 100 to 250°C, by counter-current coolant flow.

The reactor, in its most preferred embodiment, has four stages and this is effective to reduce a reformate having a CO content of 1 to 2% to below 10ppm. In other embodiments, there may be 2 to 10 stages.

The reactor is suitably in the form of a vessel in which the reaction zones are generally annular in shape, and provided with internal and/or external liquid cooling. Cooling is preferably provided by internal cooling using water, which is suitably under pressure to prevent boiling at the temperatures generated. Other liquid coolants, or forced air cooling may be used if desired. According to specific reactor designs, heat removal may be enhanced by increasing heat exchange surface areas by corrugation or other established means. Heat removal may be altered by altering the flow of coolant and/or altering the quantity of heat removed from the coolant by means of a heat exchanger.

Each reaction zone suitably comprises a metallic catalyst support ("monolith") of generally honeycomb construction, as is in common use in automobile exhaust gas catalysis. These may have 50 to 1200 cells per square in cell density, preferably 200 to 600 cpsi, and may be of a variety of types of stainless steel. In general, the present invention does not result in the reaction stages reaching the higher temperatures generally met with in exhaust gas catalysis (e.g. 500-900°C), but the material should be capable of resisting temperature excursions. An alternative reaction zone design utilises what has become known as "static mixers" which combine a very high degree of gas agitation and mixing, resulting in non-laminar flow, with relatively low pressure drop. Such static mixers may be manufactured from a variety of metals and are commercially available. However, it is presently preferred to use a honeycomb monolith.

The reaction zone desirably carries a selective oxidation catalyst comprising a platinum group metal, especially comprising platinum and/or rhodium, carried on a high

surface area metal oxide support, such as alumina. The metallic catalyst support may be coated by generally known methods with a slurry of oxide support, dried and fired, and then impregnated with the catalytically active components, before a final firing. Such procedures are in themselves known, and do not form part of this invention.

The invention will now be described with reference to the accompanying drawing which shows a cross-section of one embodiment of the present invention.

An essentially cylindrical metal vessel, made by pressing two halves and seam-welding, has a main gas inlet, 2, for reformate gas, and an outlet, 3, for cleaned gas. The vessel has a number of annular reaction zones, 4, each consisting of an annular wound corrugated catalyst support. The vessel further has an internal water jacket, 5, between a spacer and the shell and this is supplied with cooling water by means of a water circuit comprising a circulating pump, 6, and a heat exchanger, 7. The heat exchanger is desirably used to recover heat in an integrated system e.g. in an integrated combined heat and power system. The vessel further is provided with four air inlets, 8, each providing pre-determined (for a steady-state operation) levels of air (that is reaction oxygen; air is generally suitable). Although not preferred, controlled amounts of oxygen, according to one or more feedback or feed forward controls detecting gas flow levels and CO levels may be used. Downstream of each air inlet is a gas mixing zone, 9a, 9b, 9c and 9d. Zone 9a is suitably a static mixer, but zones 9b, 9c and 9d are preferably alternating annular mixing vanes, 10, and discs, 11, having gas flow holes, as illustrated in Figs 2 and 3. It should be noted that for simplicity only four vanes and four holes are shown, but more, e.g. six or eight, may be used. Such vanes and discs may be manufactured by pressing to form a sleeve which may be fitted and brazed or welded onto the jacket 5 with the intention that each gas mixing zone also serves to remove hear from the reaction gases leaving each reaction zone. Although the schematic drawing of the reactor shows each reaction zone and gas mixing zone of the same size, these may be designed to differ according to the amount of heat to be removed. Additionally, each reaction zone may incorporate different and/or different loadings, of catalyst. Each metal catalyst support monolith suitably has 300-400 cells per sq.in. and is coated with a washcoat comprising ~36wt% alumina solids of D50 of approx 5μm and D90 of approx 16μm, to deposit approx 3g/m^3. After drying and firing, the coated monolith was impregnated with

a platinum salt solution to result in 5% by wt of Pt deposited on the alumina. The resulting coated monolith was again dried and fired before being assembled into the reactor.

Initial studies indicate that a reformate containing 1-2% CO in admixture with H_2, CO_2, N_2, water vapour with a small proportion of unreacted reformer feedstock (e.g. CH_3OH, CH_4, gasoline), at 180°C may be converted to a feed gas suitable for a fuel cell, containing below 10ppm CO, and at 140°C.

The reactor of the invention is compact and exhibits relatively low pressure drop. Manufacturing costs are relatively low. The reactor is believed to be suitable for mobile or automobile uses as well as stationery uses. It is presently envisaged that the reactor shell will be lagged to control heat loss and prevent injury. The reactor can be manufactured simply and inexpensively, using pressed and welded parts. It is desirably operated to achieve low pressure drop, and the particular embodiment illustrated is designed for a gas hourly space velocity of approx. 30,000h^{-1} gas throughput.

The reactor as described may be altered in a variety of ways without departing from the central inventive concept.

The invention is now illustrated below in a working example of a two-stage reactor, fed with a synthetic reformate gas mixture containing N_2, H_2, CO, CO_2 and H_2O. Each of the two stages consists of a mixing zone with three off-set spiral vanes, followed by air injection accomplished through a number of apertures in an annular ring, producing a swirling, mixing gas. The thus mixed hydrogen and air mixture passes through an annular metal honeycomb support mounted on a central cooling jacket. The cooling jacket is fed counter-current to the flow of hydrogen with a heat transfer fluid, conveniently water under pressure, and the metal honeycomb support is mounted in good heat exchange contact with the cooling jacket. The metal honeycomb carries a selective oxidation catalyst. Gas may be extracted for analysis between the two stages and/or after the second stage. By setting the composition of the feedstock gas mixture according to that analysed after the first or second stage, the test two-stage reactor can model a three or four stage reactor.

The detailed operating conditions and other experimental detail for one typical run of the above reactor now follow. It was remarkable that the pressure drop across the whole of the est reactor was about the measurement limit of the gauges being used, and was of the order of 1.5-3mbar (150-300Pa), at the two throughputs tested. This indicates that the reactor is very efficient, compact and requires very little energy to operate.

1. Each catalyst support was an annular of internal diameter 3.85in (9.78cm), external diameter 5.85in (14,86cm) and 3.0in(7.62cm) length, made from "Fecralloy" steel and having 500 cells per sq in. Each support had been washcoated with alumina washcoat as used in exhaust gas catalytic convertors, followed by loading with 5% by wt of the alumina of Pt. Conventional manufacturing techniques were used.

2. The synthetic reformate had the compositions: 48%N_2(dry), 40%H_2 (dry), 10%CO_2(dry), 0.5-1.5%CO (dry) and 13% H_2O (of total flow). Two levels of CO concentration were chosen, a higher level to represent the output from autothermal reforming, and a lower level to represent the output from steam reformer or an optimised reformer, and two levels of throughput stated to be Nominal 3kWe (1kilowatt equivalent = 1,000 l/hr of H_2) and Nominal 6kWe, equal to 7,5000 l/hr of dry reformate and 15,000 l/hr of dry reformate respectively (8,620 l/hr and 17,240 l/hr of wet reformate).

It is plain from these results with a two-stage reformer that the compact and efficient reformer of the invention will be effective to remove CO from Hydrogen to any desired level, by conventional optimisation and especially by matching the number of stages to the requirements of the fuel cell system or other usage of the purified hydrogen.

TWO-STAGE ANNULAR SELOX REACTOR TEST RESULTS

FIRST STAGE							SECOND STAGE				
Ex No.	Power kWe	CO in %, dry	Air in, slm	Temp in C	Temp out, C	CO out %, dry	Air in, slm	Temp in, C	Temp out, C	CO out ppm dry	Sel**
1	3	1.5	4	125	212	0.60	2	167	212	1610	0.696
2	3	1.5	4	127	214	0.60	3	167	217	740	0.640
3	3	1.5	4	125	210	0.60	4	169	227	950	0.556
4	3	1.5	3	125	149	0.81	3	129	175	1840	0.684
5	3	1.5	5	128	215	0.34	3	161	220	290	0.582
6	3	0.5	2	143	176	0.122	0.5	138	145	232	0.579
7	3	0.5	2	141	167	0.122	0.8	127	136	29	0.540
8	3	0.5	2	140	161	0.122	1.0	121	130	28	0.505
9	3	0.5	2	141	172	0.122	1.2	131	146	55	0.472
10	3	0.5	1.5	142	166	?	1.0	134	157	373	0.562
11	3	0.5	2.5	142	179	?	1.0	138	150	50	0.433
12	6	0.5	4	138	167	0.130	1	148	176	722	0.520
13	6	0.5	4	138	162	0.130	2	140	185	51	0.503
14	6	0.5	4	138	166	0.130	3	146	198	105	0.428
15	6	0.5	6	138	205	62ppm	0	176	174	62	0.502

** Sel: (Selectivity) = CO consumed/2 x O_2 consumed

CLAIMS

1. A catalytic selective oxidation reactor, comprising a reactor vessel (1) with converter current cooling means (5,6,7) and at least one stage, each stage being provided with an inlet for a first feedstock (2), and inlet for a second feedstock (8), gas mixing means (9a) and a catalytic reaction zone (4).

2. A reactor according to claim1, wherein the catalytic reaction zone comprises a selective oxidation catalyst deposited upon a metal support.

3. A reactor according to claim 2, wherein the metal support is mounted in good heat exchange contact with the cooling means.

4. A reactor according to any one of the preceding claims, wherein the cooling means comprises a central jacket mounted within the reactor.

5. A reactor according to any one of the preceding claims, having from 2 to 10 stages.

6. A reactor according to claim 5, having four stages.

7. A reactor according to any one of the preceding claims, connected to the output from a reformer such that CO is removed from the output gas to a level where the output from the reactor may be fed to a fuel cell.

8. A process for the removal of quantities of CO from a hydrogen feedstock by partial oxidation, comprising at least one step of admixing said feedstock with a quantity of oxygen, passing the resulting mixture over a selective oxidation catalyst in a selective oxidation zone and recovering a hydrogen product with reduced content of CO, whilst simultaneously cooling the selective oxidation zone by counter-current coolant flow.

9. A process according to claim 8, wherein the selective oxidation zone is maintained at a temperature in the range 100 to 250°C.

10. A process according to claim 8 or 9, providing hydrogen to fuel a fuel cell.

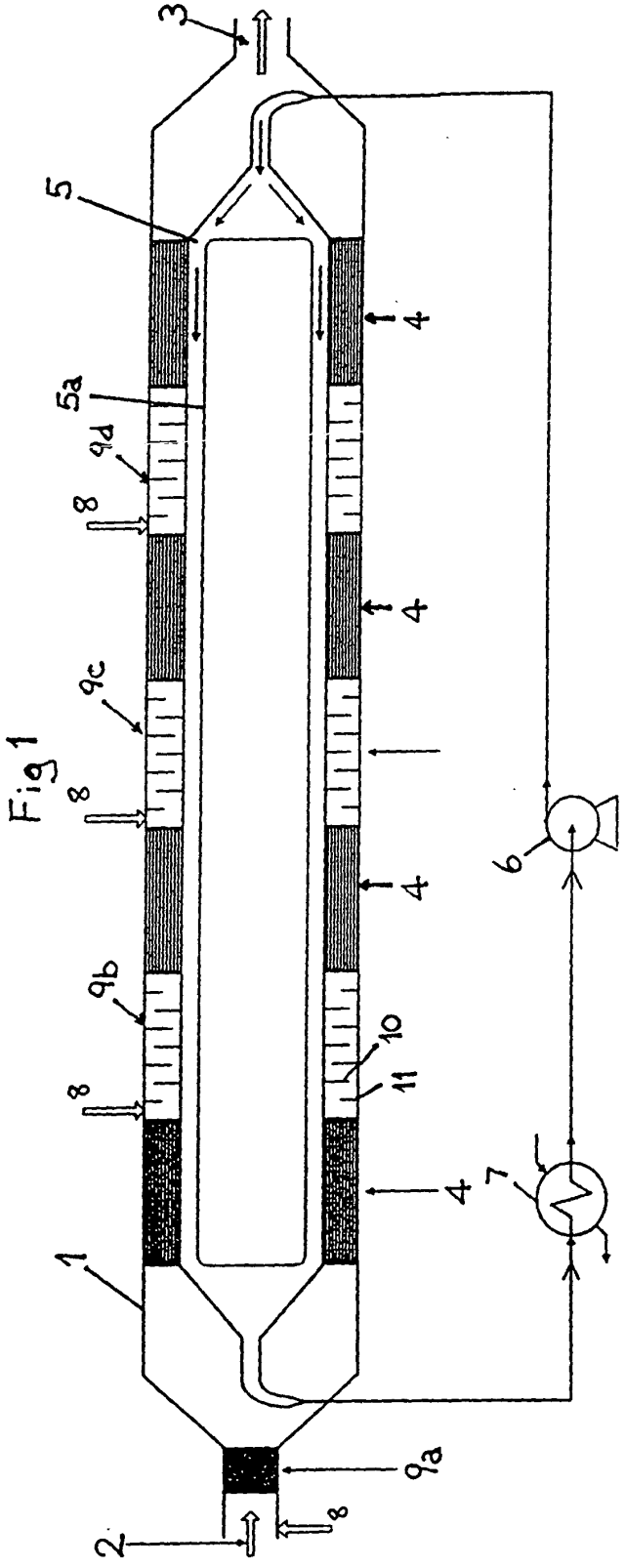

Fig 1

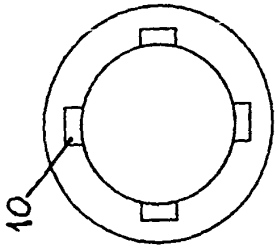

Fig 3

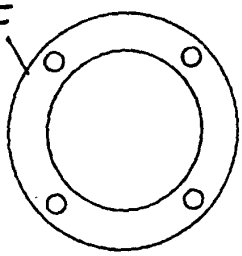

Fig 2

INTERNATIONAL SEARCH REPORT

Inter onal Application No
PCT/GB 99/03958

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B3/58 B01J19/24 B01J8/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 19005 A (INT FUEL CELLS CORP) 30 September 1993 (1993-09-30) page 9, line 2 -page 12, line 32 figure 1	1,4,5, 7-10
X	DE 195 44 895 C (DAIMLER BENZ AG) 27 February 1997 (1997-02-27) column 2, line 23 - line 47 column 3, line 35 -column 4, line 50	1-3,5-10
X	GB 2 075 859 A (HUMPHREYS & GLASGOW LTD) 25 November 1981 (1981-11-25) claims; figures	1,4-6
X	US 4 988 431 A (HEISEL, M ET AL.) 29 January 1991 (1991-01-29) claims; figure	1,4,5

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 February 2000	

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van der Poel, W

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INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/GB 99/03958

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 43 34 981 A (DAIMLER BENZ AG) 20 April 1995 (1995-04-20) the whole document ---	1,2,5-10
A	EP 0 305 203 A (TOPSOE HALDOR AS) 1 March 1989 (1989-03-01) page 3, line 37 - line 63 page 4, line 19 - line 21 page 4, line 51 - line 61 -----	

INTERNATIONAL SEARCH REPORT

information on patent family members

Int[illegible]ional Application No
PCT/GB 99/03958

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9319005 A	30-09-1993	US 6010675 A	04-01-2000
		DE 69325092 D	01-07-1999
		DE 69325092 T	30-09-1999
		EP 0631564 A	04-01-1995
		EP 0873967 A	28-10-1998
		US 5330727 A	19-07-1994
DE 19544895 C	27-02-1997	EP 0776861 A	04-06-1997
		US 5874051 A	23-02-1999
GB 2075859 A	25-11-1981	NONE	
US 4988431 A	29-01-1991	DE 3631642 A	07-04-1988
		CA 1295815 A	18-02-1992
		DE 3775672 A	13-02-1992
		EP 0260530 A	23-03-1988
		US 5084247 A	28-01-1992
DE 4334981 A	20-04-1995	EP 0650923 A	03-05-1995
		US 5674460 A	07-10-1997
EP 0305203 A	01-03-1989	DK 448187 A	28-02-1989
		CA 1304215 A	30-06-1992
		DE 3885545 D	16-12-1993
		DE 3885545 T	10-03-1994
		JP 1139137 A	31-05-1989
		JP 2592662 B	19-03-1997
		NO 883826 A,B,	28-02-1989
		US 4985230 A	15-01-1991

MMC MMC

PATENT COOPERATION TREATY

09/857116

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:
Wiehart, Ian Carmichael
JOHNSON MATTHEY TECHNOLOGY CENTRE
Blounts Court
Sonning Common
Reading RG4 9NH
GRANDE BRETAGNE

RECEIVED
16 MAR 2001

NOTIFICATION OF TRANSMITTAL OF INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Applicant's or agent's file reference: PFC 1436 PCT	Date of mailing (day/month/year): 09.03.2001
	IMPORTANT NOTIFICATION

International application No.	International filing date (day/month/year)	Priority date (day/month/year)
PCT/GB 99/03956	29/11/1999	01/12/1998

Applicant: JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Netherlands Tel.: (+31-70) 340-2040. Tx. 31 651 epo nl Fax: (+31-70) 340-3016	VAN DER POEL

Form PCT/IPEA/416 (July 1992) P20473 (07/03/2001)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
JPC 1436 PCT		
International application No.	International filing date (day/month/year)	Priority date (day/month/year)
PCT/GB 99/03958	29/11/1999	01/12/1998
International Patent Classification (IPC) or national classification and IPC		
C01B3/58		
Applicant		
JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 8 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 9 sheets.

3. This report contains indications relating to the following items:

   I ☒ Basis of the report

   II ☐ Priority

   III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

   IV ☐ Lack of unity of invention

   V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

   VI ☐ Certain documents cited

   VII ☒ Certain defects in the international application

   VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
23/06/2000	09.03.2001
Name and mailing address of the IPEA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Netherlands Tel. (+31-70) 340-2040, Tx. 31 651 epo nl Fax: (+31-70) 340-3016	VAN DER POEL

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/03958

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-6 as originally filed

Claims, No.:

1-14 as received on 18/09/2000 with letter of 12/09/2000

Drawings, sheets:

1/1 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

see separate sheet

4. Additional observations, if necessary:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/03958

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-14
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-14
Industrial applicability (IA)	Yes:	Claims	1-14
	No:	Claims	

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Re Item I
Basis of the report

1. With his reply to the first written opinion the applicant has filed a completely new set of claims, without referring to this fact in his letter of reply. Of course, due to this omission to mention the new set of claims, also no basis for the amendments has been indicated.

   This is highly objectionable, because it puts a high burden on the examiner to find all the amendments, and to further find their basis in the application as filed.

2. Some of the amendments proposed by the applicant go beyond the application as filed (Article 34(2)(b) PCT).

2.1. Claim 6 defines that the central jacket is connected via a coolant circuit to a circulating pump. The basis for this amendment seems to lie in page 3, lines 11-13, where a water circuit and a circulating pump are disclosed.

   This has now been generalised to cooling circuit in general. Subject-matter has been added.

   It is admitted that on page 2 it is mentioned that other coolants can be used. However, the circulating pump seems only to be disclosed in relation to water being the coolant.

2.2. Claim 10 defines that the gas mixing means comprise annular mixing vanes or discs. The expression "annular mixing vanes or discs" can only be found on page 3, lines 20 and 21. This passage discloses that the first mixer is a static mixer, whereas the other mixers are alternating "annular mixing vanes or discs".

   The claims now specifies that also the first mixer is an "annular mixing vane or disc", which was not disclosed in the application as originally filed. Subject-matter has been added.

2.3. Since the applicant has not given any indication of the basis for the amendments,

the final decision on the allowability of the amendments is deferred to the regional phase.

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: WO-A-93/19005
D2: GB-A-2075859
D3: US-A-4988431
D4: DE-A-19544895

1. The subject-matter of the present claims is novel. The subject-matter of claims 1-14 does not involve an inventive step, however (Article 33(3) PCT).

Inventive step objections arise starting from document D1 and starting from document D4.

1.1. Starting from document D1:

Document D1 discloses a reactor for the selective oxidation of carbon monoxide in the presence of hydrogen. The reactor contains two catalytic beds. Cooling coils are embedded in the 2 catalyst beds. From figure 1 it is clear that the coolant flows countercurrently to the reacting stream. The reactor has inlets for gaseous fuel and oxygen. The product from the reactor is fed to a fuel cell (see figure 1; page 9, line 3 - page 12, line 32).

In his letter of reply of 12.09.2000, the applicant has argued that claim 1 is novel for several reasons.

Firstly, it is argued that the present reactor is contained in a single vessel. With respect, the examiner cannot agree on this point of view, because claim 1 specifies that the reactor comprises a cylindrical reactor vessel, with at least one

stage. Document D1 clearly has one stage in a vessel. The presence of a second stage in a second vessel is certainly not excluded from claim 1.

Secondly, it is argued that the apparatus of document D1 does not have any mixing means. With respect, the examiner cannot agree with the applicant here. It should first be mentioned that the term mixing means is extremely broad, giving no indication what sort of mixer is meant. In any case, on page 9, lines 20-23 of document D1 disclose that the perforated support member (23) facilitates distribution of gases to all regions of the catalyst bed. Perforated support member (23), therefore, clearly functions as a mixing means.

The only difference between claim 1 and document D1, therefore, lies in the fact that in claim 1 the catalyst is supported on a metallic support, whereas in document D1 the catalyst is supported on a metal oxide support.

Document D4 discloses an apparatus for the selective oxidation of carbon monoxide. The catalysts used in this apparatus are preferably supported on a metallic support.

The person skilled in the art will certainly consider using catalysts supported on a metallic support in the apparatus of D1. The subject-matter of claim 1 does not involve an inventive step.

It is noted that similar objections can be raised starting from document D2 and document D3.

1.2. Starting from document D4:

Document D4 discloses an apparatus and process for the selective oxidation of carbon monoxide in presence of hydrogen. The apparatus has several catalytic stages, in which the catalyst is preferably supported on metallic supports. The reactor is cooled by a cooling circuit, which is connected to the outside of the reactor. From the figures, it would appear that the cooling takes place co-currently. The reactor has inlets for oxygen and for the gas to be treated and contains several static mixers to achieve mixing (and cooling) of the reactants.

The product of the reactor can be fed to a fuel cell (see figures; column 3, line 35 - column 4, line 50).

The only difference between claim 1 and document D4 lies in the fact that in claim 1 the cooling takes place countercurrently, whereas in document D4 the cooling takes place co-currently.

The skilled chemical engineer, who is the person skilled in the art in the present case, always considers both co- and countercurrent operation of heat-exchange processes.

The applicant has argued that claim 1 further differs from document D4 in the fact that in claim 1 the apparatus is cylindrical, whereas in document D4 this would not be the case. The examiner cannot agree on this point with the applicant. Although the preferred embodiment of document D4 is directed to a plate-type reactor, the use of other forms for the reactor are also disclosed according to the examiner. In any case, the choice of a cylindrical shape for a reactor is the first choice for the skilled chemical engineer, for the reasons as given by the applicant in his letter of reply to the written opinion (compact, easy manufacture).

The subject-matter of claim 1 does not involve an inventive step.

2. The subject-matter of claim 12 does not involve an inventive step.

Document D1 is considered to be the closest prior art for claim 12.

The only difference between claim 12 and document D1 lies in the fact that in claim 1 the catalyst is supported on an annular metal support, whereas in document D1 the catalyst is supported on a particulate metal oxide support.

Document D4 discloses the use of metallic supports in the selective oxidation of carbon monoxide.

The person skilled in the art will, therefore, certainly think of using a metallic catalyst support. The further choice of an annular shape of the support, seems to

be the choice from a limited number of possibilities.

The subject-matter of claim 12 does not involve an inventive step.

3. The subject-matter of claims 2-11, 13 and 14 also does not involve an inventive step.

3.1. Claims 2, 4-7 are directed to features of the cooling of the reactor, which are all well-known measures to the person skilled in the art. The subject-matter of claims 2, 4-7 does not involve an inventive step.

3.2. A recent trend in gas-phase catalytic reactions is the use monoliths as catalyst supports. The subject-matter of claim 3 does not involve an inventive step.

3.3. Both document D1 and document D4 disclose a plurality of oxidation stages. The person skilled in the art will be able to choose the optimum number of stages. The subject-matter of claims 8 and 9 does not involve an inventive step.

3.4. The mixing vanes or discs seem to be well-known mixing means. The subject-matter of claim 10 does not involve an inventive step. It is noted that the claim does not fulfil the requirements of Article 34(2)(b) PCT (see section I, above).

3.5. From the introduction of document D4 it is clear that the selective oxidation of carbon monoxide is used on synthesis gas, to make it suitable for use in a fuel cell. The subject-matter of claims 11 and 14 does not involve an inventive step.

3.6. Document D1 discloses using an inlet temperature of 320°F (=160°C; see claim 11). The subject-matter of claim 13 does not involve an inventive step.

Re Item VII

Certain defects in the international application

1. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1 and D4 is not mentioned in the description, nor are these documents identified therein.

CLAIMS

1. A catalytic selective oxidation reactor, comprising a cylindrical reactor vessel (1) with counter current cooling means (5,6,7) and at least one stage, each stage being provided with an inlet for a first feedstock (2), and inlet for a second feedstock (8), gas mixing means (9) and a catalytic reaction zone (4), wherein the reaction zone comprises a selective oxidation catalyst deposited upon a metal support.

2. A reactor according to claim1, wherein the metal support is mounted in good heat exchange contact with the cooling means.

3. A reactor according to any one of the preceding claims, wherein the metal support is a metal monolith.

4. A reactor according to any one of the preceding claims, wherein the cooling means comprises a central jacket mounted within the reactor.

5. A reactor according to claim 4, wherein the central jacket is connected via a coolant circuit to an external heat exchanger.

6. A reactor according to claim 4 or 5, wherein the central jacket is connected via a coolant circuit to a circulating pump.

7. A reactor according to any one of the preceding claims, wherein the catalytic reaction zone(s) is/are annular and surround a central cooling means.

8. A reactor according to any one of the preceding claims, having from 2 to 10 stages.

9. A reactor according to claim 8, having four stages.

10. A reactor according to any one of the preceding claims, wherein the gas mixing means comprise annular mixing vanes or discs.

11. A reactor according to any one of the preceding claims, connected to the output from a reformer such that CO is removed from the output gas to a level where the output from the reactor may be fed to a fuel cell.

12. A process for the removal of quantities of CO from a hydrogen feedstock by partial oxidation, comprising at least one step of admixing said feedstock with a quantity of oxygen, passing the resulting mixture over a selective oxidation zone comprising a selective oxidation catalyst on an annular metal support, and recovering a hydrogen product with reduced content of CO, whilst simultaneously cooling the selective oxidation zone by counter-current coolant flow.

13. A process according to claim 12, wherein the selective oxidation zone is maintained at a temperature in the range 100 to 250°C.

14. A process according to claim 12 or 13, providing hydrogen to a fuel cell.